

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, DC 20460

OFFICE OF PREVENTION, PESTICIDES, AND TOXIC SUBSTANCES




06/20/12


MEMORANDUM

SUBJECT: HeiQ AGS-20 Surface Area Determination: Review and Assessment of
The Study

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| PC Code(s):072599 | DP Barcode(s)/No(s): 402176 |
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From: A. Najm Shamim, PhD, Chemist 
Risk Assessment & Science Support Branch
Antimicrobials Division (7510P)

Thru: Jed Costanza, PhD
Regulatory Management Branch 1
Antimicrobials Division (7510P)

To: Nader Elkassabany, PhD, Chief 
Risk Assessment & Science Support Branch
Antimicrobials Division (7510P)

Performing Lab: Micrometrics Analytical Services, Norcross, GA 30093
Lab Project #: PR120316-001; PR120308-10
Sponsor: HeiQ materials AG, Zurcherstrasse 42, Switzerland

Background

HeiQ submitted their product AGS-20 for registration with the Agency. The registrants had claim of nanosilver in their product. The Agency granted a conditional registration to AGS-20 in Dec. 2011. As part of the conditional registration the Agency required HeiQ to submit many studies related to the characterization of their product. The Agency asked HeiQ to submit the product characterization methods for their product. HeiQ submitted protocols in this regard and suggested that they will characterize their product by the following methods (AD Memo by N Shamim, Feb. 28, 2012) :

1. In the process of surface area characterization of the AGS-20, HeiQ will employ: BET Method through Nitrogen absorption. This is a standard and the most common method applied for surface area determination
2. Oxygen pulse chemisorption Method: This method will help in determining the exposed surface area of silver metal particles within a silica matrix. A method from a published work will be used to generate data for this part.
3. STEM: To obtain a composite image through electron beam when the sample is in a rastering pattern. Three magnifications to be used: low, medium and high. Particle size distribution of AGS-20 and silver metal will be determined.
4. SEM: When electron beam move across the surface and the reflected electrons provide images of external particle structure). Low magnification will be used. Size distribution of AGS-20 particles will be determined.
5. Light Scattering Sample suspended in water will be analyzed for the particle size distribution of the suspended particles,
6. Powder XRD Method: Will provide phase composition, grain size, orientation, epitaxy, defect structure and film thickness. This is an X-ray diffraction method. An average of silver particle size will be determined through this technique.

The Agency reviewed and accepted the protocols. The present submission from the registrants consists of characterization data of AGS-20 based on number 1 and 2 methods listed above.

Specific Surface Area (SAA) determination for the product AGS-20.

The present submission consists of two parts: a) Determination of the surface area of AGS-20, which is the composite of fused silica and silver particles by applying nitrogen adsorption BET method; b) Determination of surface area of the nanosilver particles

within the composite of the fused silica and silver particles by making use of Oxygen Pulse Chemisorption method.

A. Detailed Discussion:

1a:

Nitrogen adsorption isotherm measurement is carried by the application of the principles of the classical Brunauer, Emmett and Teller (BET) method. A sample of the material under consideration is transferred into a vacuumed tube and under vacuum is transferred into area where it is exposed to liquid nitrogen under increasing pressures. As the pressure changes, more gas is absorbed on the surface of the material under consideration till it reaches a maximum at which point a bulk condensation is achieved. A reverse process of desorption will take place when the gas starts to be released with decreasing pressure. The adsorption/desorption processes will generate isotherms which in turn reveal surface and internal pore characteristics of a material. The samples were run in triplicate and the results were averaged.

1b:

Oxygen Pulse Chemisorption study was conducted based on the published work referred by the registrants in their protocol submission. By this method the surface area of the silver particles is determined. The process consisted in providing oxygen pulses to generate oxygen adsorption isotherms. There are a number of assumptions made in the application of this technique:

- a) Assumed silica particles do not interact with oxygen.
- b) Assumed all silver particles on the composite material interact with oxygen.
- c) Adsorption of oxygen is independent of the crystalline structure of silver.
- d) Oxygen will interact with silver in the ratio of: 2 Ag: O

The sample is dried under nitrogen atmosphere, followed by reduction in hydrogen stream at 350 °C, and finally flushed with helium gas. The study itself is conducted at 150 °C under helium atmosphere. For each pulse of oxygen given, amount of oxygen absorbed is quantified. The instrument of the study is called Micrometrics AutoChem II 2920.

1c:

Results from BET Experiments:

[REDACTED]

1d:

Results from Pulse Oxygen Chemisorption Experiment:

[REDACTED]

B. RASSB Conclusions and Recommendations

1. RASSB finds the submission to be deficient as a number of details are missing. Only the results have been included in the submission. The important factors missing: a) method descriptions are not outlined; b) experimental set ups are not discussed.; c) sensitivities of methods are not described; d) the actual experimental running conditions, instrument make if applicable, model etc. for both methods Are not included in the study report.
2. The results from the two methods have provided some useful information to the Agency.
3. BET provides adequate data about the surface area of the product AGS-20
4. A number of uncertainties exist for oxygen chemisorptions study: a) to determine the diameter of silver present in the product it is assumed that it has spherical shape, where as nanosilver is known to exist in various shapes (and hence the diameter will be different); b) the sorption of oxygen on the fused silica surface as well as on the product AGS-20 could be physio-sorption or chemisorption; the study author has assumed that only chemisorption will take place. No explanation is provided why physio-sorption will not occur.
5. RASSB, therefore, recommends:
 - a) HeiQ address uncertainties as discussed in # 4
 - b) Provide details of experimental set up for the studies as indicated in # 1.
 - c) Generate data and submit the studies for the last four methods as listed above

At this time RASSB considers this as an incomplete submission.